



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

Kanako TANAKA, ET AL.

Serial No. Application of 10/608,262

Filed: June 30, 2003

For: DYE FIXING AGENT FOR WATER-COLOR INK, IN JET RECORDING MEDIUM
AND POROUS HYDROTALCITE COMPOUND

Hon. Commissioner of Patents and Trademarks
Washington, D.C. 20231

D E C L A R A T I O N

I, TANAKA Kanako, am one of the co-inventors of U.S. Patent Application Serial No. 10/608,262 and well familiar with the content of the invention thereof. I have read Office Action dated February 9, 2005 issued by the Examiner in the U.S. Patent Application Serial No. 10/608,262.

For demonstrating clear differences between the invention of U.S. Patent No. 4351814 (Miyata et al) cited by the Examiner and the present invention, I carried out the following experiments.

I. Purpose and tenor in experiments

Hydrotalcite is to be synthesized by tracing all of Examples 1, 2, 4 and 5 of U.S. Patent No. 4351814 (Miyata et al) as faithfully as possible, and the thus-obtained hydrotalcite is to be measured for a specific surface area.

II. Contents of experiments

Experiments II-(1) to II-(5) described below correspond to Examples 1, 2, 4 and 5 as follows. In Example 2 of U.S. Patent No. 4351814 (Miyata et al), two types of hydrotalcite are synthesized, so that the Example 2 is separated to a first half

and a second half.

<u>Experiment No.</u>	<u>Example No. of Miyata et al</u>
II-(1)	Example 1
II-(2)	First half of Example 2
II-(3)	Second half of Example 2
II-(4)	Example 4
II-(5)	Example 5

Experiment II-(1)

Eight liter of an aqueous solutions of a mixture of 2.3 moles/liter of magnesium chloride and 0.4 mole/liter of calcium chloride was adjusted to a temperature of about 20°C, and 136 g of powdery calcium hydroxide was added. The mixture was fully stirred for about 10 hours. Insoluble materials were removed by filtration, and the filtrate was allowed to stand at room temperature for 90 hours to precipitate needle-like crystals. The product was heated to 100°C, and aged at this temperature for 4 hours, and thereafter further aged at room temperature for 3 days. The resulting needle-like crystals were separated by filtration, washed fully with water, and dried.

Water (700 ml) and 7.3 ml of sodium aluminate ($\text{Al}^{3+}=5.43$ moles/liter, $\text{NaOH}=9.54$ moles/liter) were put into a 1-liter autoclave, and the aforesaid water-washed needle-like magnesium chloride was added (pH 12.8). The mixture was hydrothermally treated at 120°C, for 4 hours with stirring. The amount of the sodium aluminate added corresponded to about 1 equivalent of the chlorine contained in the basic salt. The product was taken out (pH=11.8) from the autoclave, filtered, washed with water, dehydrated, and dried.

The product obtained was a hydrotalcite compound. The BET specific surface area (m^2/g) of the hydrotalcite compound was measured and the result was shown in Table 1 below.

Experiment II-(2)

To 14 liters of ion bittern ($\text{MgCl}_2=1.63$ moles/liter,

$\text{CaCl}_2=0.705$ mole/liter) at 20°C was added 46 g (corresponding to an $\text{MgO}:\text{MgCl}_2$ mole ratio of 1:20) of magnesium oxide. With stirring, the mixture was heated to 90°C . When the temperature of the mixture reached 90°C , the heating was stopped, and the mixture was allowed to stand at 20°C for 70 hours to precipitate needle-like crystals. The crystals were again heated to 80°C , and aged at this temperature for 30 minutes, followed by filtration and washing with water. The water-washed crystals were dried. The water-washed product $[\text{Mg}_3(\text{OH})_2\text{Cl}\cdot 4\text{H}_2\text{O}]$ was suspended in 500 ml of water, and the suspension was well stirred. Aluminum chloride (0.03 mole) was added to the suspension and completely dissolved. The solution was heated to 60°C , and 200 ml of sodium carbonate (0.8 mole/liter) was added ($\text{pH}=11.5$). The mixture was maintained for about 30 minutes (the pH after equilibrium was 10.2). The product was then allowed to cool to room temperature, filtered, washed with water, dehydrated, and dried. The dried product was a hydrotalcite compound. The BET specific surface area (m^2/g) was measured and the result was shown in Table 1 below.

Experiment II-(3)

The water-washed product $[\text{Mg}_3(\text{OH})_2\text{Cl}\cdot 4\text{H}_2\text{O}]$ obtained by the same method of the above Experiment II-(2) (8 g calculated as a dried product) was suspended in 500 ml of water at room temperature, and with sufficient stirring, 0.016 mole of ferric sulfate was added. The temperature of the mixture was raised to about 70°C , and sodium hydroxide was added to adjust the pH of the mixture to 12.5.

The mixture was then stirred for about 1 hour, whereupon the pH of the mixture reached an equilibrium at 11.5. The product was filtered, washed with water, dehydrated, and dried. The dried product was a hydrotalcite compound. The product was found to have the approximate chemical composition $\text{Mg}_{0.8}\text{Fe}_{0.2}(\text{OH})_2(\text{SO}_4)_{0.1}\cdot 0.6\text{H}_2\text{O}$.

The BET specific surface area (m^2/g) of the hydrotalcite obtained was measured and the result was shown in Table 1 below.

Experiment II-(4)

To 10 liters of an aqueous solution of magnesium chloride (40 mole/liter) was added 104 g of magnesium oxide having a purity of 93 % at about 20°C. With stirring, the mixture was heated to about 70°C. Then the heating was stopped, and the mixture was allowed to cool to room temperature for about 1 day, then again heated to 40°C, and maintained at this temperature for 4 days. Then, a part of the resulting compound was filtered and washed with water. When the washed compound was dried, it was basic magnesium chloride in needle-like crystals having the composition $\text{Mg}_2(\text{OH})_3\text{Cl} \cdot 4\text{H}_2\text{O}$.

The water-washed compound $\text{Mg}_2(\text{OH})_3\text{Cl} \cdot 4\text{H}_2\text{O}$ obtained above was suspended in about 5 liters of water, and with stirring, 0.6 mole of ferric nitrate was added and completely dissolved. The solution was heated to 60°C, and 3 moles/liter of sodium hydroxide was added to adjust the pH at equilibrium to 10.5. To the resulting system was further added 0.3 mole of sodium tartrate, and the mixture was stirred for about 30 minutes. The resulting product was filtered, washed with water, dehydrated, and dried. The dried product was a hydrotalcite.

The BET specific surface area (m^2/g) of the hydrotalcite obtained was measured and the result was shown in Table 1 below.

Experiment II-(5)

414 g of $\text{Mg}_2(\text{OH})_3\text{Cl} \cdot 4\text{H}_2\text{O}$ prepared by the method of the above Experiment II-(4) was suspended in about 5 liters of water, and with stirring, 0.86 mole of chromium nitrate was added and completely dissolved. The solution was heated to about 40°C, and sodium hydroxide (5 moles/liter) was added until the pH at equilibrium reached about 10. To the resulting system was further added 0.3 mole of potassium ferrocyanide, and the mixture was stirred for about 30 minutes. The product was filtered, washed with water, dehydrated, and dried. The dried product was a hydrotalcite.

The BET specific surface area (m^2/g) of the hydrotalcite obtained was measured and the results shown in Table 1 below.

III The measurement of the BET specific surface area:

The BET specific surface area (m^2/g), of a hydrotalcite compound (particles) are obtained from the absorption of N_2 gas with the NOVA 2000 gas adsorption device of Quantachrome Co., Ltd. after a measurement sample was maintained at 110°C 1.3Pa or less for 3 hours as a pre-treatment.

The BET specific surface area (m^2/g), of the hydrotalcites obtained by Experiment II-(1) to II-(5) are shown in Table 1 below.

Table 1

Experiment No.	BET specific surface area (m^2/g)
II-(1)	36
II-(2)	17
II-(3)	38
II-(4)	37
II-(5)	33

IV. Conclusion

The following can be understood from the results of the above Table 1

(a) Hydrotalcite samples obtained according to all of Examples of U.S. Patent No. 4351814 (Miyata et al) have a BET specific surface area of 38 (m^2/g) at the largest.

(b) Miyata et al neither teach anything concerning any hydrotalcite containing a specific silicic acid ion (HSi_2O_5^-) as an anion in the formula (1), nor did they obtain any such a hydrotalcite. I am of the opinion that Miyata et al had no intention to obtain a porous hydrotalcite compound.

(c) It is concluded that that Miyata et al does not disclose any method (process) for producing a porous hydrotalcite having a BET specific surface area of 50 (m^2/g) or more, and that Miyata

et al did not obtain any such hydrotalcite.

The undersigned declarant further declares that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of the application or any patent issuing thereon.

The 18th of April, 2005

Kanako Tanaka

Kanako TANAKA

CD-ROM JCPDS (卡式形式)

25-1430

25-1430

Quality : 1

Cu Al4 S O4 (OH) 12 . 8 H2 O

Cu₁₂S₈Al₄(OH)₁₆(SO₄)₁₂ · 12.8H₂O

Copper Aluminum Sulfate Hydroxide Hydrate

Chalcoalumite

Rad : CrK α Lambda : 2.29090 Filter : Beta d_{sp} : Debye-Scherrer

Cutoff : Int : film densitometer reading (Film (dens.)) 1/1cor :

Ref : Mineral. Rec.

2 126 1971 Williams. Ehin.

Sys : Monoclinic, b axis

S.G. : P21 (4)

a : 17.09000 b : 8.82000 c : 10.22000 A : 1.91692 C : 1.14574

A : B : 95.580 C : Z : 4 MP :

Ref :

Dx : 2.250 Dm : 2.290 SS/FOM : F(28)=4.3 (0.048000.126)

ea : nvd : ey : Sign : 2V :

Ref :

Unit cell from single crystal study, refined from powder data.

Light blue

Specimen from Bisbee, Arizona, USA.

Plus 14 additional reflections to 1.191.

d-value	Int	h	k	l	d-value	Int	h	k	l
8.5000	100	2	0	0					
7.9000	20	1	1	0					
6.7100	9	0	1	1					
6.3800	8	-1	1	1					
6.1000	8	1	1	1					
5.4500	8	-2	1	1					
5.1000	13	2	1	1					
4.7900	20	3	1	0					
4.5700	8	-2	0	2					
4.5100	6	-1	2	0					
4.2500	90	4	0	0					
4.1800	25	2	0	2					
3.8500	3	4	1	0					
3.7100	5	-4	1	1					
3.5000	6	-3	2	0					
3.3400	6	-1	2	2					
3.1800	9	5	1	0					
3.0600	8	-2	1	3					
2.8220	6	-1	8	1					
2.7260	8	-2	3	1					
2.6330	8	-3	8	0					
2.5850	7	-6	0	2					
2.5200	11	1	3	2					

CD-ROM JCPDS (卡片形式)

41-1428

41-1428

Quality : 0

Mg6 Al2 (C O8) (O H)16 . 4 H2 O

Magnesium Aluminum Carbonate Hydroxide Hydrate

Hydroxalcite

Rad : Lambda : 1.54050

Filter :

d_sp : Diffractometer

Cutoff : Int : Diffractometer

1/1cor :

Ref : Acta Mineral. Sinica

1984 296 1984 Jiang, S., Zhang, G., Liang, H., Huang, W.

Sys : Rhombohedral

S.G. : R-3m (166)

a : 6.15100

b :

c : 46.50000

A : 7.55975

C :

Ref :

B :

C :

Z : 8

mp :

Dx : Dm : 2.040

SS/FOK : F(20)=0.8 (0.172000.158)

ea :

nwb :

ey :

Sign :

2V :

Ref :

Specimen from Jianshibao asbestos mine, Sichuan, China.

Chemical analysis (wt.%): VA12 O3V 17.18, VC12 O3V 0.68, MgO 39.67,

VC O2V 7.22, YH2 OY61 35.14, NiO 0.12, K Mg5.98, X10.01 5.99

(Al2.04 . CrO.05)2.09 (O H)16 C O3 13.87 H2 OY.

Light red

To replace 14-191 and 22-700.

O assigned because four reflections are unindexed.

d-value	Int	h	k	l	d-value	Int	h	k	l
16.1160	55	0	0	3					
7.8440	100	0	0	6					
4.3410	10	0	0	0					
3.9140	80	0	1	8					
2.8350	5	0	1	14					
2.7710	5	0	0	0					
2.6080	30	0	2	4					
2.5160	10	0	0	0					
2.4020	3	1	1	12					
2.3700	9	0	0	0					
2.3110	9	0	2	10					
2.1980	10	0	0	21					
2.1910	9	1	1	15					
2.0280	12	2	1	1					
1.9730	9	1	1	18					
1.9570	10	0	2	16					
1.8620	15	2	1	10					
1.6640	4	0	2	22					
1.5760	12	1	0	28					
1.5400	6	3	3	0					
1.5060	7	2	2	6					
1.3040	10	4	0	7					
1.2540	5	1	2	29					
1.1720	9	2	3	11					